RC3: 'Comment on egusphere-2023-1242', Anonymous Referee #3, 03 Aug 2023

Hong et al examine two pollution episodes in Xiamen, China characterized by elevated PM and ozone. They look at the impact of formaldehyde on both, using a box model to demonstrate the role of HCHO on hydroxymethanesulfonate formation in PM2.5 and the importance of HCHO on ozone production. While the authors do a fine job of presenting their results, the main weakness of this paper is the strong dependence on a box model without any attempts at validation or discussion of the potential limitations/uncertainties. Before publication, concerns related to this issue, outlined in more detail below, and other minor points need to be addressed.

Response: Thank you very much for all the valuable comments and good suggestions. We have addressed each comment in the following point by point and have revised the manuscript accordingly.

Indeed, we didn't present the details of the box model analysis, and have also limited discussion of its potential limitations/uncertainties. Here, we make enough supplement for the related materials of the box model, according to your good suggestions.

The Observation-based model (OBM)

A chemical box model, as one of the important methods for analyzing atmospheric chemical processes, was run based on the platform of the Framework for 0-Dimensional Atmospheric Modeling (F0AM), which has broad application potential in deeply exploring atmospheric observation data and comprehensively understanding the regional atmospheric pollution. About the chemical mechanism, the F0AM incorporating the latest chemical mechanism version of MCM-v3.3.1 (MCM, http://mcm.leeds.ac.uk/MCM/, last access: 13 May 2022) was applied to simulate the detailed photochemical processes and quantify the reaction rates of HCHO mechanism, and the MCM mechanism introduced 142 VOCs and about 20,000 chemical reactions.

About the uncertainties of the model simulation results, the index of agreement (IOA) was used to judge the reliability of the model simulation results, as follows:

$$IOA = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(|O_i - \bar{O}| - |S_i - \bar{O}|)^2}$$

where *Si* is simulated value, *Oi* represents observed value, $\bar{O}$ is the average observed values, and n is the sample number. The IOA range is 0-1, and the higher the IOA value is, the better agreement between simulated and observed values is. In this study, the simulation results (the IOA is approximately 0.80) are reasonable, and the performance of the OBM-MCM model was acceptable.

Uncertainty evaluation of aqueous HCHO analysis:

Since aqueous HCHO was not available during the observation, which was the key chemical components influencing the subsequent HMS modeling, we established the aqueous HCHO concentrations by the mass transfer processed between the gas- and particle- phase. Among this processes, the uncertainties were introduced somehow by the Henry's law constant adopted in the model. We conducted a sensitivity test with 2 folds of current used Henry's law constant of HCHO, with a value of 6×10^7 M atm^{-1}. As shown in Fig S0, the modeled aqueous HCHO as well as HMS concentrations increased with the increase of Henry's law constant in the sensitivity case, with increase of 0.01 and 0.13 μg m^{-3} for aqueous HCHO and HMS, respectively. It is quite reasonable considering the increased solubility of HCHO. On the other hand, the modeled HCHO and HMS were still exhibited higher concentrations during the pollution episodes (EP1 and EP2), of which higher precursors and favorable aerosol properties enhanced the heterogeneous processes. Therefore, the impacts of HCHO Henry's law constant approximations on the conclusions are supposed to be minor.

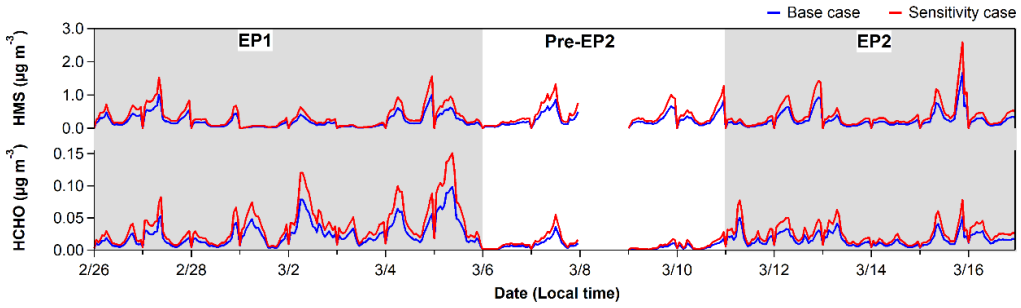

Fig S0. Time series of the modeled aqueous HCHO and HMS concentrations with the model used Henry's law constant of HCHO (referred as base case, the blue line) and 2 folds of the model used Henry's law constant of HCHO (referred as sensitivity case, the red line), respectively.

Line 85: I am unfamiliar with HMS, as I imagine, will be many of the readers of this paper. More background should be given as to the importance and relevance of this species in the introduction.

Response: Thank you for your good suggestions. We have added the details of the HMS in the revised manuscript, as follows:

HMS is an important organosulfur compound in the atmosphere, not only in cloud and fog but also in atmospheric aerosols (Munger et al., 1986; Dixon and Aasen, 1999). The misidentification of HMS as inorganic sulfate caused the overestimation of the observed particulate sulfate (Ma et al., 2020; Dovrou et al., 2022).

Recent studies have shown that HCHO can react with hydrogen peroxide (H_2O_2) to produce hydroxymethyl hydroperoxide (HMHP), which rapidly oxidizes dissolved sulfur dioxide (SO_2, aq) to sulfate (Dovrou et al., 2022). Meanwhile, HCHO reacts

with dissolved SO_2 (aq) to produce hydroxymethanesulfonate (HMS, $HOCH2SO^-$), which, upon oxidation with the hydroxyl radical (OH), forms sulfate (Ma et al., 2020; Moch et al., 2018, 2020).

Dixon, R. W. and Aasen, H.: Measurement of hydroxymethanesulfonate in atmospheric aerosols, Atmos. Environ., 33, 2023–2029, https://doi.org/10.1016/s1352-2310(98)00416-6, 1999.

Munger, J. W., Tiller, C., and Hoffmann, M. R.: Identification of hydroxymethanesulfonate in fog water, Science, 231, 247–249, https://doi.org/10.1126/science.231.4735.247, 1986.

Line 106: You introduce the term "observation-based model" analysis here like it is a standard term. You need to explain here that this is the name of the modeling framework that you are using for this study.

Response: Thank you for your kindly comments. We have added the details of the OBM model in SI.

A chemical box model, as one of the important methods for analyzing atmospheric chemical processes, was run based on the platform of the Framework for 0-Dimensional Atmospheric Modeling (F0AM), which has broad application potential in deeply exploring atmospheric observation data and comprehensively understanding the regional atmospheric pollution. About the chemical mechanism, the F0AM incorporating the latest chemical mechanism version of MCM-v3.3.1 (MCM, http://mcm.leeds.ac.uk/MCM/, last access: 13 May 2022) was applied to simulate the detailed photochemical processes and quantify the reaction rates of HCHO mechanism, and the MCM mechanism introduced 142 VOCs and about 20,000 chemical reactions (Jenkin et al., 2003).

Jenkin, M.E., Saunders, S.M., Wagner, V., Pilling, M.J., 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. Atmos. Chem. Phys. 3, 181–193.

Line 117: Since your study is focused on Feb – Mar, isn't the average RH and T for that time period more relevant than the annual average.

Response: Thank you for your good suggestions. We have revised the sentence, as follows:

It is situated in a subtropical monsoon climate, with an average temperature of 18.5°C and a relative humidity of 63.3% during the wintertime observation.

Line 132: Information about the uncertainties of your observations is needed, particularly for formaldehyde.

Response: Thank you for your comments. We have added the details of measured air pollutants in TableS3, as follows:

Table S3. The detection limits, time resolutions and measured uncertainties of air pollutants

Species	Measurement Techniques	Uncertainties	Detection limits	Time resolution
HCHO	FMS-100, Focused Photonics Inc., Hangzhou, China	≤5%	50 pptv	1 s
PAN	PANs-1000, Focused Photonics Inc., Hangzhou, China	±10%	50 pptv	5 min
O_3	Model 49i, Thermo Fischer Scientific, USA	±5%	1 ppbv	1 h
NOx	Model 42i, Thermo Fischer Scientific, USA	±10%	0.5 ppbv	1 h
CO	Model 48i, Thermo Fischer Scientific, USA	±5%	40 ppbv	1 h
SO_2	Model 43i, Thermo Fischer Scientific, USA	±10%	0.5 ppbv	1 h
VOCs	GC-FID/MS, TH-300B, Wuhan, China	±10%	20-300 pptv	1 h
HONO	MARGA, ADI 2080, Applikon Analytical B.V., the Netherlands	±20%	50 pptv	1 h

Line 155: 23:00 local time?

Response: Thanks. We have replaced it with 11:00 pm.

Line 167: What's the resolution of the ERA reanalysis and how dependent are your results on the accuracy of the PBL height? I would imagine deposition in your model could be quite sensitive to the accuracy of this term.

Response: Thank you for your good suggestions. The resolution of ERA-5 reanalysis is 0.25°×0.25°.However, the BLH data was only used to explain the diffusion conditions during different pollution levels of $PM_{2.5}$ and O_3. As you mentioned that, there exists potential uncertainties if they are considered as constraints data. Therefore, we didn't input them into the OBM model. The related sentences have been revised as follows:

According to our previous studies, the model incorporates the physical process of deposition within the boundary layer height (BLH), which varies from 300 m during nighttime to 1500 m during the daytime in winter (Li et al., 2018;Liu et al., 2022).

Line 195: I'm confused as to why you are using boundary layer heights from autumn when your study is based on Feb. – Mar.

Response: Thank you for your comments. Corrected.

Section 2.4: I agree with the other reviewer that more details about this model are needed. I assume this is a box model, although you never say that explicitly. How do you handle NO/NO2 constraints in this model? Are they both constrained to observations and held constant? Is NOx constrained as a family like in other box models (e.g. F0AM, DSMACC)? The handling of NOx will have considerable impact on your discussion of ozone production so more details are required here.

Response: Thank you for your good suggestions and comments. We have presented the details of the box model analysis, and made correspondingly the supplement for the related materials of the box model in the revised manuscript and SI.

As the reviewer mentioned, the NOx will have considerable impacts on the production of O_3. We used the observation data of NO and NO_2 in the real environment to handle NO/NO_2 constraints in this model (Line 222-225), according to our previous studies (Liu et al., 2022a,b). So, in this study, NOx constrained as a family is not applied for the box models.

Liu, T., Hong, Y., Li, M., Xu, L., Chen, J., Bian, Y., Yang, C., Dan, Y., Zhang, Y., Xue, L., Zhao, M., Huang, Z., and Wang, H.: Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model, Atmos. Chem. Phys., 22, 2173-2190, 10.5194/acp-22-2173-2022, 2022a.

Liu, T., Lin, Y., Chen, J., Chen, G., Yang, C., Xu, L., Li, M., Fan, X., Zhang, F., and Hong, Y.: Pollution mechanisms and photochemical effects of atmospheric HCHO in a coastal city of southeast China, Sci. Total Environ., 160210, https://doi.org/10.1016/j.scitotenv.2022.160210, 2022b.

Line 212: To what time-scale are you interpolating?

Response: Thanks. The observation data with 1h time resolution were interpolated to constrain the OBM model.

Line 221: What meteorology are you using and at what resolution?

Response: Thank you for your comments. Meteorological data used here were obtained from the Global Data Assimilation System (GDAS) with a 1°×1°spatial resolution and 3-h temporal resolution.

Line 223: You need to include a citation for cluster analysis.

Response: Thanks. Corrected.

Line 302: I might have missed it, but I don't think you ever defined what SOR and NOR mean.

Response: Thanks for your suggestions. Corrected.

Line 324: More information about the HCHO + H2O2 reaction is needed here. How easily does this reaction happen in ambient air, ie, is there actually significant production of hydroxymethyl hydroperoxide from this reaction? Is this a gas phase or aqueous phase reaction?

Response: Thanks for your suggestions. We have added the details of HCHO + H_2O_2 reaction in SI, as follow:

In the atmosphere, gaseous HCHO with high Henry's law constant can partition into aerosol or cloud/fog water, then the aqueous HCHO can reacts with H_2O_2 to form HMHP, with an upper bound forward rate constant of 100 (±35) M^{-1} s^{-1} and reverse rate constant of 0.6 (±0.2) s^{-1}(Dovrou et al.,2022). In the gas phase, HMHP is mainly formed by the hydration of CH_2OO Criegee radicals and then can partition into aerosol water, which have the potential to oxidize SO_2(aq) to form sulfate. From the perspective of contributions of HMHP paths to sulfate formation, the researcher revealed that the HCHO-catalysis path (HCHO + H_2O_2) under fast equilibrium is more significant than HMHP-direct path (hydration of CH2OO in the gas-phase) to global sulfate, so HCHO-catalysis path is significant for HMHP production. So, in the future, we will carry out the observation of H_2O_2 for further evaluate the effects of HCHO + H_2O_2 reaction on the HMHP production.

Dovrou, E., Bates, K. H., Moch, J. M., Mickley, L. J., Jacob, D. J., and Keutsch, F. N.: Catalytic role of formaldehyde in particulate matter formation, P. Natl. Acad. Sci. USA, 119, e2113265119, 10.1073/pnas.2113265119, 2022.

Section 3.4: Here is where more investigation is needed. While I realize that you don't have aqueous phase measurements of HCHO, you need to present some form of evaluation of your model or at the very least an uncertainty analysis to put the accuracy of your results in context. Are there previous studies you can cite that use this model that can reproduce observations of any of the species you are modeling here? How do

measurement uncertainties affect your results? If you perturb your input HCHO by its uncertainty, how does that change your aqueous phase HCHO, for example? How is gamma determined in your model? Is it just a set value or is it parameterized in the model somehow? How does uncertainty in gamma affect your results? What's the uncertainty in the Henry's law constant for HCHO? Etc.

Response: Thank you for your good comments and suggestions. We have added the sentences in the revised manuscript.

Exactly, the lack of aqueous phase measurements of HCHO would introduce uncertainties somehow to the model simulation and the corresponding results. Before we initiated the aqueous HCHO and HMS modeling, we carefully considered the establishment and the reproduce of aqueous HCHO, which was the key steps for further HMS modeling. Since the Henry's law constant is the key parameter for HCHO partitioning, we noted that the theoretical value provided by the CAPRAM would not suitable for current aerosol particle modeling and might resulted the underestimate of aqueous HCHO, as many recent studies pointed out that the field-derived effective Henry's law constants of HCHO are almost several orders of magnitude (10^4 - 10^6) higher than the theoretical values, also HCHO in ambient particle phase have been found several orders of magnitude higher than that predicted by the traditional theories. Therefore, we concluded the field-derived effective Henry's law constants of HCHO from the recent published studies, which mainly in the order of 10^7 M atm^{-1} at ambient temperatures (~296 K) during the observation period. We finally selected a middle value provided by Mitsuishi et al. (2018) with a value 3.1×10^7 M atm^{-1}. We performed the sensitivity analysis to evaluate the uncertainties introduced by the Henry's law constant of HCHO, details were added into the supplement materials. Here in brief, we used 2 folds of the HCHO Henry's law constant as the sensitivity case and conducted the simulation of the aqueous HCHO as well as HMS concentrations. We found that aqueous HCHO and HMS exhibited slight higher concentrations due to the increased solubility of HCHO, with increases of 0.01 and 0.13 μg m^{-3} for HCHO and HMS, respectively. However, the modeled HCHO and HMS were still exhibited higher concentrations during the pollution episodes (EP1 and EP2), which still able to support our major conclusions. On the other hand, we compared our modeling aqueous HCHO concentrations with previous observations. As shown in the following tables, our modeling aqueous HCHO concentrations are comparable and in the same order of magnitude with previous observations. Therefore, uncertainties due to the lack of aqueous HCHO measurement and the HCHO Henry's law constant approximations would take minor impacts on our major conclusions.

Table. Comparison of modeled aqueous HCHO concentrations with previous observations

Aqueous HCHO concentration (ng m^{-3})	References
18	this study
28	Andrade et al., 1995
18	Odabasi et al., 2005
40	Klippel et al., 1980
23	Shen et al., 2018

Andrade, J. B. D.; Pinheiro, H. L. C.; Andrade, M. V. A. S. d., The Formaldehyde and Acetaldehyde Content of Atmospheric Aerosol. Journal of the Brazilian Chemical Society 1995, 6, 287-290.

Odabasi, M.; Seyfioglu, R., Phase partitioning of atmospheric formaldehyde in a suburban atmosphere. Atmospheric Environment 2005, 39, (28), 5149-5156.

Klippel, W.; Warneck, P., The formaldehyde content of the atmospheric aerosol. Atmospheric Environment (1967) 1980, 14, (7), 809-818.

Shen, H. Q.; Chen, Z. M.; Li, H.; Qian, X.; Qin, X.; Shi, W. X., Gas-Particle Partitioning of Carbonyl Compounds in the Ambient Atmosphere. Environmental Science & Technology 2018, 52, (19), 10997-11006.

Figure 4: You need to indicate which of these panels are from observations and which are output from your model.

Response: Thank you for your kindly suggestions. We have revised the Figure 4 and rewritten the sentences.

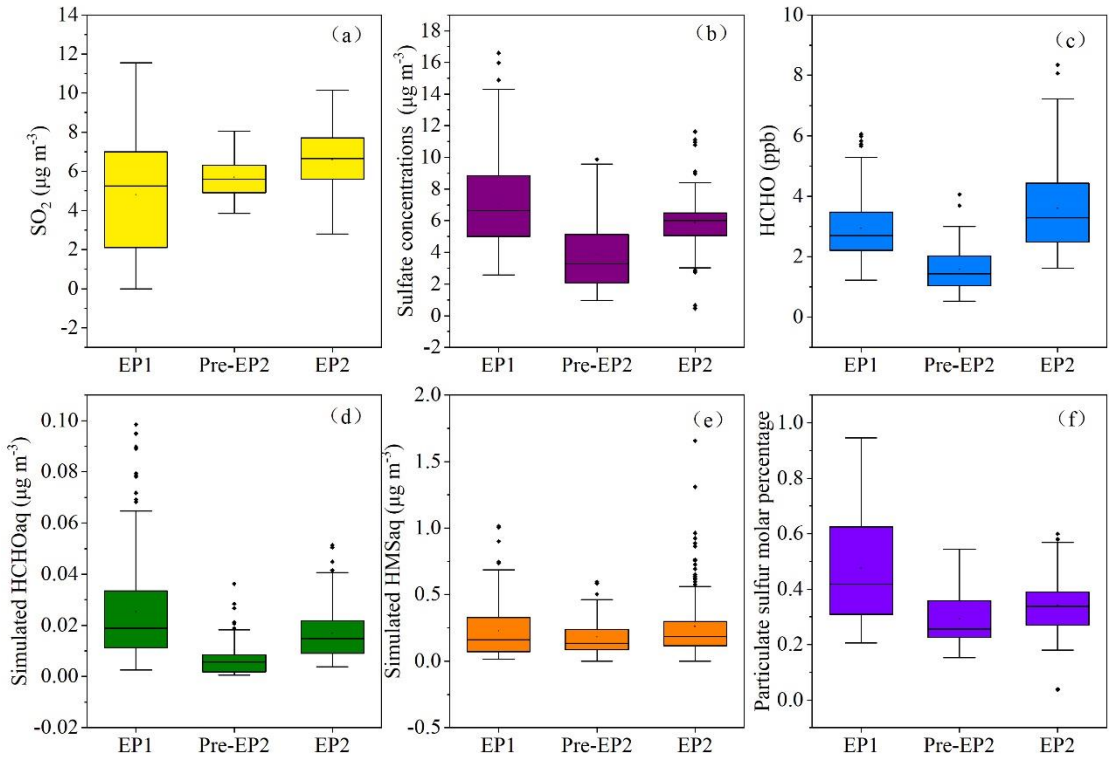

Figure 4. Concentrations of SO_2, SO_4^{2-}, and HCHO observed at different pollution stages. The simulated HCHO (aq) and HMS (aq) were also presented. The particulate sulfur molar percentage was calculated as $[n(SO_4^{2-})+n(HMS)]/[n(SO_4^{2-})+n(HMS)+n(SO_2)]$. In the box–whisker plots, the whiskers, boxes, and points indicate the 5th/95th, 25th/75th, 50th percentiles, and mean values.

Line 350: “through” is mis-spelled.

Response: Thanks. Corrected.

Line 354 and 359: HCHO (aq) and HMS were not directly observed, correct? You only calculate it with your model. Please don’t use the word “observed” when you are talking about model output.

Response: Thank you for your good suggestions. We have revised the related sentences.

Section 3.5: My comment about model validation extends to this section as well, although it is less concerning given that your results are broadly consistent with other studies.

Response: Thank you for your kindly comments and suggestions. About the uncertainties of the model simulation results, the index of agreement (IOA) was used to judge the reliability of the model simulation results, as follows:

$$IOA = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(|O_i - \bar{O}| - |S_i - \bar{O}|)^2}$$

where *Si* is simulated value, *Oi* represents observed value, $\bar{O}$ is the average observed values, and n is the sample number. The IOA range is 0-1, and the higher the IOA value is, the better agreement between simulated and observed values is. In this study, the simulation results (the IOA is approximately 0.80) are reasonable, and the performance of the OBM-MCM model was acceptable.

Line 377: I'm unclear as to what you mean by input HCHO and non-input HCHO. As well as when, in the abstract for example, you say you "disabled the HCHO mechanism". Are you just not constraining your model to observed HCHO? Are you removing all reactions that produce or remove HCHO from the chemical mechanism? Please explain this more clearly.

Response: Thank you for your good comments.

To furtherly quantify the varieties in ROx chemistry and O_3 formation in response to HCHO chemistry, two parallel scenarios were conducted through the F0AM model. One scenario was run with all MCM mechanism defined as Input HCHO mechanism, and the other was run with the HCHO mechanism disabled in MCM mechanism defined as Non-input HCHO mechanism. Considering the numerous chemical formation reactions of HCHO, our study mainly disabled the HCHO loss pathways of HCHO photolysis, HCHO + OH, and HCHO + NO_3, which makes HCHO become a stable secondary pollutant that will not continue to react, thus the HCHO loss pathways were disabled in Non-input HCHO mechanism scenario. The differences in ROx levels and production pathways in the two model scenarios were analyzed to investigate the chain effect of HCHO on ROx cycling and O_3 formation. More details could be found in our previous studies (Liu et al., 2023).

These sentences have been added into the revised manuscript, as follows:

To furtherly quantify the effects of HCHO on ROx chemistry and O_3 formation, we disabled the loss pathways of HCHO photolysis, HCHO + OH, and HCHO + NO_3 in MCM mechanism, defined as Non-input HCHO mechanism (Liu et al., 2023). Meanwhile, the other scenario was run with all MCM mechanisms, defined as Input HCHO mechanism.

Liu, T., Lin, Y., Chen, J.*, Chen, G., Yang, C., Xu, L., Li, M., Fan, X., Zhang, F., and Hong, Y.* Pollution mechanisms and photochemical effects of atmospheric HCHO in a coastal city of southeast China. *Science of the Total Environment*. 2023, 859:160210